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CITATION:

Hyon, Suong Hyu ...[et al]. Structure and Physico-Chemical Properties of Polyvinyl Alcohol, Stretched at the Amorphous State and Annealed (Special Issue on Polymer Chemistry XI). Bulletin of the Institute for Chemical Research, Kyoto University 1975, 53(4): 367-380

ISSUE DATE:

1975-11-29

URL:

http://hdl.handle.net/2433/76631

Bull. Inst. Chem. Res., Kyoto Univ., Vol. 53, No. 4, 1975

Structure and Physico-Chemical Properties of Polyvinyl Alcohol, Stretched at the Amorphous State and Annealed

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Received May 14, 1975

A stretching mode of polyvinyl alcohol film in the swollen state without crystallinity is examined. Comparison is made of the physico-chemical properties as well as the crystalline structure between samples which were prepared either by this process or by the usual stretching in the dry state with crystallinity. It is confirmed by X-ray diffraction and differential scanning calorimetric techniques that the former sample has a highly ordered and stable crystalline phase in the structure with very high melting and shrinking temperatures. The melting temperature rises in accordance with increasing of the stretching degree and a characteristic dual peek appears in the fusion curve for samples stretched more than 3 times. The temperature where detectable shrinkage appears with heating (shrinking temperature) is about 40°C higher than for the latter sample.

INTRODUCTION

The stretching or drawing that is one of important processes in manufacturing of synthetic or man-made fibers to produce molecular orientation along the fiber axis can be achieved in a temperature range between the glass transition and melting temperatures of the material polymers. It is evident as exemplified in the fiber forming processes of various fibers that this process should be performed in the absent of the crystallinity or at least in a reduced crystalline state of the polymers to promote the molecular orientation and obtain excellent fiber properties. However, in the industrial manufacturing of Vinylon from polyvinyl alcohol (hereafter, abbreviated as PVA), the stretching is necessarily conducted at high temperatures in the presence of the crystallinity after spinning, during which the crystallization of the polymer takes place to some extents due to the high crystallizable ability.

That whether the crystallinity exists or not in stretching process will have extremely enhanced effects not only in promoting of molecular orientation but also in forming of the crystalline structure. For example, it was found[1~7] that, if a lightly cross-linked polyethylene is crystallized after stretching or compressing at the melt; namely in the absent of crystallinity, a very unique crystalline structure is produced with extra ordinarily high melting temperature and excellent transparency. In this structure polymer molecules in the crystalline region are highly ordered in the three-dimensional space in accordance with the macroscopic deformation at the melt but those in the amorphous region are rather disordered and exhibit high degree of mobility.[2,7]

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This is thought to be caused by the fact that the state of the molecules stretched in the amorphous state is elastically maintained until the crystallization occurs and the crystallization is performed from the stretched molecules. The similar phenomena are observed for various polymers such as isotactic polypropylene[8,9] and polyvinyliden fluoride.[10]

The above-cited result is not expected generally unless chemically cross-linked points exist in the structure since the deformation in the amorphous state cannot be held. However, even in the case of PVA without cross-linking points a similar result elastically may be expected if the polymer is stretched in the swollen or amorphous state, because the molecules of the polymer have rather strong intermolecular attractive forces due to the hydrogen bond formation and entanglement effects of molecules.

In this paper a mode of stretching of PVA in a swollen state without crystallinity and following crystallization is studied under the expectation mentioned above.

EXPERIMENTAL

Material

A fraction with a viscosity-average molecular weight of 1.45×10^5 was obtained from a commercial PVA from the Kuraray Co. with a listed viscosity-average molecular weight of 77,000 and degree of saponification of 99.94%. Intrinsic viscosity measurements were made in water at 80°C, and molecular weights were calculated using the relation $[\eta]=9.4\times10^{-4}\,M^{0.56}$ of Matsuo and Inagaki.[11] About 0.3 mm-thick film was obtained from the 10% aqueous solution according to a routine casting technique. The degree of crystallinity of this film was evaluated to be 0.38 by the density measurement.

Stretching and Annealing

a. Stretching in Swollen State (Swell-Drawing). The sample film was immersed in water at 60°C for 5 minutes and stretched to various predetermined extents with a rate of stretching of 500%/sec. and then it was transferred into methanol at 60°C or acetone at 50°C with the length held constant and dried *in vacuo* and finally annealed at a temperature of 220°C for 2 minutes. In the above the sample swelled in water to about 1.6 times the original volume and no crystallinity was detected by an X-ray diffraction analysis but it exhibited rubbery elasticity for high degrees of stretching. It is supposed that in the above-described processes molecular chains in the sample were stretched with no crystallization and the crystallization was carried out from the stretched molecular chains. The degree of stretching was characterized by the ratio of film lengths after and before stretching. This draw ratio ranged from 1 to 7.

b. Stretching in Non-Swollen State at High Temperatures (Heat-Drawing). The sample film was stretched in air at temperatures of 120°C or 180°C and annealed at 220°C for 2 minutes with the length held constant.

Density and Degree of Crystallinity

The density measurement was made at 30°C by a density gradient column of

benzene and tetrachlorocarbon. In this measurement to avoid effects from air bubbles sample was dipped in benzene *in vacuo* and transferred into the gradient column. The density was also converted to the degree of crystallinity using the relation $1/\rho=(X/\rho_c)+(1-X)/\rho_a$. Here, ρ, ρ_c, and ρ_a designate the experimentally observed density and densities at the perfectly crystalline and amorphous states of the polymer, respectively. ρ_c and ρ_a were taken as 1.345 and 1.269.[12] X designates the degree of crystallinity.

Birefringence

The birefringence was obtained by measuring the retardation of sample at room temperature in white light with polarized light microscope using the Bereck compensator.

X-ray Diffraction

The radiograph was taken with a 114.6-mm powder camera, with Ni-filtered Cu Kα radiation, and with the film fixed asymmetrically. A number of *d*-spacings of the crystal planes of the monoclinic crystalline form of the polymer were determined. The errors due to film shrinkage and radius deviation of the camera were corrected using forward and backward diffractions of NaF compounded in the sample.[13]

Fusion and Enthalpy Change in Fusion

The fusion curve was obtained by a differential scanning calorimetry with use of the Perkin Elmer DSC 1–B by a heating rate of 10°C/min. The amount of the sample used was about 3–4 mg and the correction of temperature was made with use of 99.99% pure Indium. The melting point was defined to be a temperature where the fusion finally terminated. The enthalpy change in the fusion was estimated by planimetry of the fusion curve with a reference datum for purified benzoic acid.

Dynamic Modulus

The dynamic modulus was measured at room temperature by a dynamic viscoelastometer Vibron DDV–2 from the Toyo Baldwin Co. at a frequency of 110 cps.

Shrinkage with Heating

The dimensional change with increasing temperature in the direction of stretching was measured in air and water at a constant load of 1 g/mm^2. The change in the length with heating of 0.5°C/min was read off by a cathetometer, and expressed in percents by dividing with the original length.

RESULTS AND DISCUSSION

According to the procedure described in the experimental section the molecular fraction of PVA used in this work could be stretched to high extents in the swollen state in water without breaking. Figure 1 shows the X-ray diffraction photograph for the sample stretched sixfold and annealed. It indicates very high degree of molecular orientation as well as high degree of crystallinity. It is concluded, therefore, that

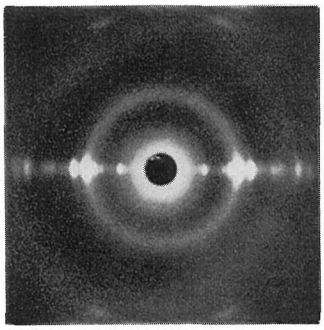

Fig. 1. Wide angle X-ray photograph of the PVA film stretched sixfold in the swollen state and annealed. The photograph was taken with X-ray perpendicular to the stretching direction (meridian of the pattern).

although the sample without cross-linked points was stretched in the swollen amorphous state molecular chains in the structure were stretched in accordance with the macroscopic deformation and the stretched state of molecular chains was maintained until major crystallization took place by annealing. Note here that, if the starting commercial unfractionated PVA with the lower average-molecular weight was dipped in water at 60°C in the same manner, partial dissolution of the sample took place and no stretching could be achieved. The stretching in the swollen state could be performed only for a sample with high molecular weights, where intermolecular attractive forces due to hydrogen bond formation and entanglement effects of polymer chains prohibit plastic flow of molecular chains and reserve the rubbery elasticity just like as chemical cross-linkings for other polymers such as polyethylenes.[1~3]

In any case in this preparing mode of sample the crystallization is thought to have been brought about from stretched amorphous chains. On the other hand since the sample film has a degree of crystallinity of about 38% in the non-swollen state, the usual stretching in air at high temperatures should involve many complicated phenomena such as stretching of molecular chains in the amorphous region and crystallization of those, orientation of the crystalline region or crystallites, partial melting of the crystallites and recrystallization of those, and *etc.* Thus, the crystalline structures and hence various properties of the samples that are prepared by these two kinds of stretching; the swell-drawing and heat-drawing, are thought to be quite different with each other. In fact we have confirmed various characteristic properties for the former sample. In the following sections we will show and discuss the data, considering the detailed crystalline structure of samples.

Density and Crystallinity

Figure 2 shows the density and degree of crystallinity for samples stretched under various conditions and those further annealed. Here, closed and open triangles indicate data for the swell-drawn samples, before and after annealing. The squares and circles indicate data for the heat-drawn samples before and after annealing as detailed explanations are given in the caption of the figure. As can be seen by the triangle data, when the sample is stretched in the swollen state and dried the crystal-

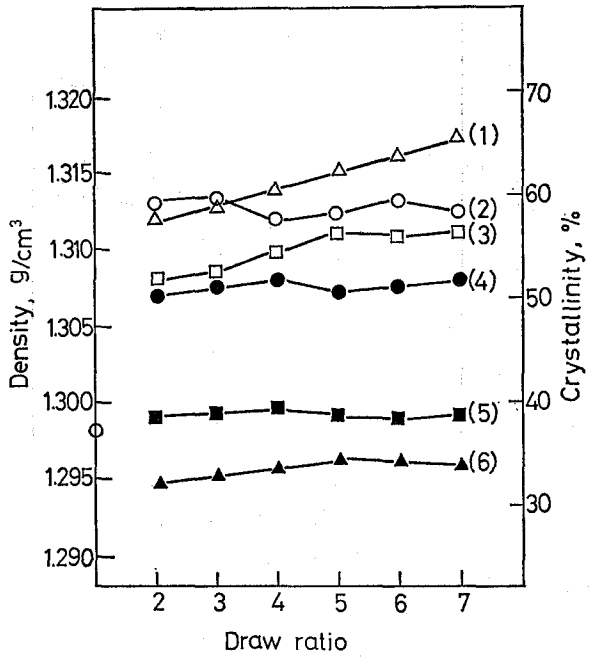

Fig. 2. Density and crystallinity *vs.* draw ratio for drawn PVA films. Curves; (1) stretched in the swollen state and annealed, (2) stretched at 180°C in air and annealed, (3) stretched at 120°C in air and annealed, (4) stretched at 180°C in air and not annealed, (5) stretched at 120°C in air and not annealed, (6) stretched in the swollen state and not annealed.

linity does not appear so much. It remains almost constant at less than 34% with increasing of stretching. But by annealing at 220°C it conspicuously increases proportionally with increasing of the draw ratio, reaching 66% at sevenfold stretching (data indicated by open triangles). Contrary, when the sample is stretched in air at high temperatures the crystallization proceeds appreciably during stretching but it does not reach so high level by annealing. The degree of crystallinity of the annealed samples stays almost constant or slightly increases with increasing of draw ratio so that it cannot go over 59%. We note here that the degree of crystallinity of 66% for the sevenfold stretched and annealed sample is the highest among data reported for atactic PVA up to date.[12)]

Birefringence

The birefringence of samples stretched under different conditions with subsequent annealing is plotted in Fig. 3 against draw ratio. Increase of the birefringence with increasing of draw ratio is most pronounced for the sample stretched in the swollen state. The sevenfold swell-drawn sample is associated with the largest birefringence of about 4.5×10^{-2} that indicates the highest degree of molecular orientation along stretching direction. Since as will be discussed later the molecular orientation in the amorphous region in this sample is not thought to be so enhanced, the highest molecular orientation should be contributed by the molecular alignment in the crystalline region; namely by the highly oriented crystalline region or crystallites in good agree-

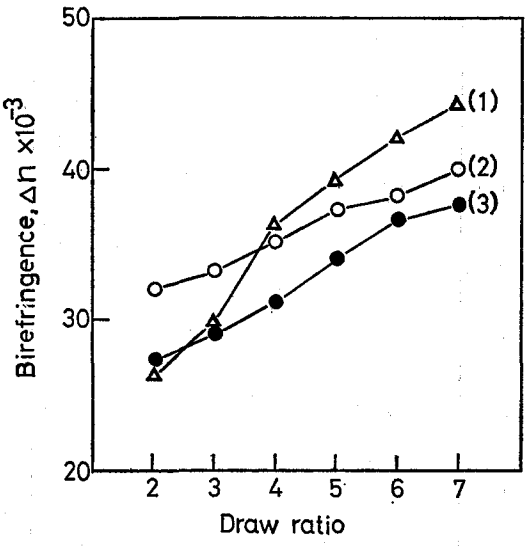

Fig. 3. Birefringence *vs.* draw ratio for drawn PVA films. Curves; (1) stretched in the swollen state and annealed, (2) stretched at 180°C in air and annealed, (3) stretched at 120°C in air and annealed.

ment with the suggestion from its X-ray photograph shown in Fig. 1.

Crystallographic Parameters

The *d*-spacings for various crystal planes for samples made in the different manners are listed in Table I. It can be seen that either the sample is stretched in the swollen state or in the non-swollen state in air, the *d*-spacings of various crystal planes (h01) aligned parallel to the stretching direction shrink as draw ratio increases. Contrary, when PVA sample is stretched to high extents at high temperatures in a usual manner, expansion of the crystallographic unit-cell has been sometimes reported,[14~16] but no such expansion is recognized but shrinkage is observed.

Based on the *d*-spacings for (200), (002), and (20$\bar{1}$) or (201) of the sevenfold heat-

Table I. *d*-Spacings in *A*° of Drawn PVA Films Obtained by X-ray Powder Camera Samples

(hkl)	5-fold stretched in air at 120°C and annealed	7-fold stretched in air at 120°C and annealed	5-fold stretched in swollen state and annealed	7-fold stretched in swollen state and annealed
100	7.900	7.830	7.830	7.762
001	5.608	5.505	5.471	5.471
10$\bar{1}$	4.671	4.599	4.575	4.599
101	4.484	4.396	4.396	4.352
200	3.986	3.917	3.900	3.900
20$\bar{1}$	3.290	3.243	3.231	3.231
201	3.143	3.110	3.110	3.110
002	2.788	2.739	2.730	2.730

drawn and swell-drawn samples, the unit-cell parameters are calculated as, $a=7.842$, $c=5.484$ Å with $\beta=92.55°$ for the former sample and $a=7.808$, $c=5.466$ Å with $\beta=92.55°$ for the latter sample. Here, described are the average values of the parameters estimated with use of the d-spacing of (201) or (20$\bar{1}$). Since the unit-cell dimension b parallel to the molecular chain axis and stretching direction is thought to stay unaltered, if b is taken to be 2.52 Å which was experimentally determined by Sakurada and others[14] and two vinyl alcohol groups are assumed to be packed in the unit-cell, the unit-cell density will be estimated to be 1.341 and 1.352 for the heat-drawn and the swell-drawn samples, respectively.

The data shown here should indicate excellent perfection of the crystalline phase in the structure for the swell-drawn sample which has been stretched in the swollen state and annealed, comparing with the data for the heat-drawn sample and referring to the crystallographic data reported up to date.[14~18]

Fusion Behavior

The fusion curves obtained with the Perkin Elmer DSC 1–B for samples made by stretching in air at 120°C and subsequence annealing are shown in Fig. 4. As draw ratio is increased, the temperature where major fusion occurs and the melting point arise. Note here that a small shoulder associated with the fusion peak for the highest stretched samples is detectable in the low temperature side of the peak. Appearance of similar small shoulder has been recognized by Mochizuki and others[19] with a DTA measurement for stretched PVA samples. It should indicate a heterogeneity or dual crystalline structure in samples, but the shoulders in the figure are too weak so that no further consideration is allowable. However, for the PVA samples made by stretching in the swollen state the dual crystalline structure is distinctly recognized. As is shown in Fig. 5, each of the curves for these samples consists of well-isolated two peaks. One appears at temperatures of 234.7, 235.1, and 235.7°C, respectively for the three-, five-, and seven-fold stretched samples in a range of temperatures little higher than

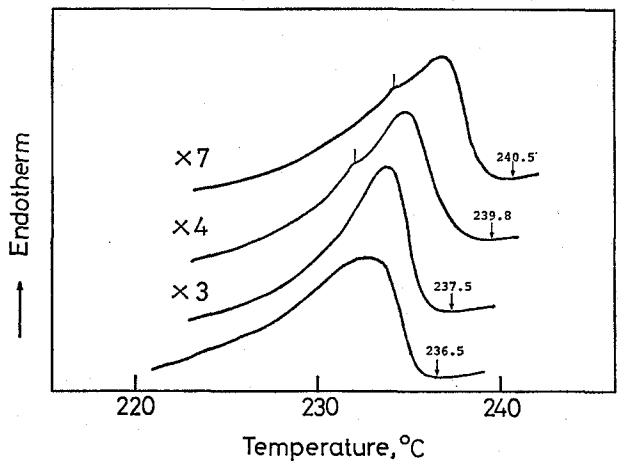

Fig. 4. DSC thermograms for PVA films stretched at 120°C and annealed. The draw ratio is indicated to each curve.

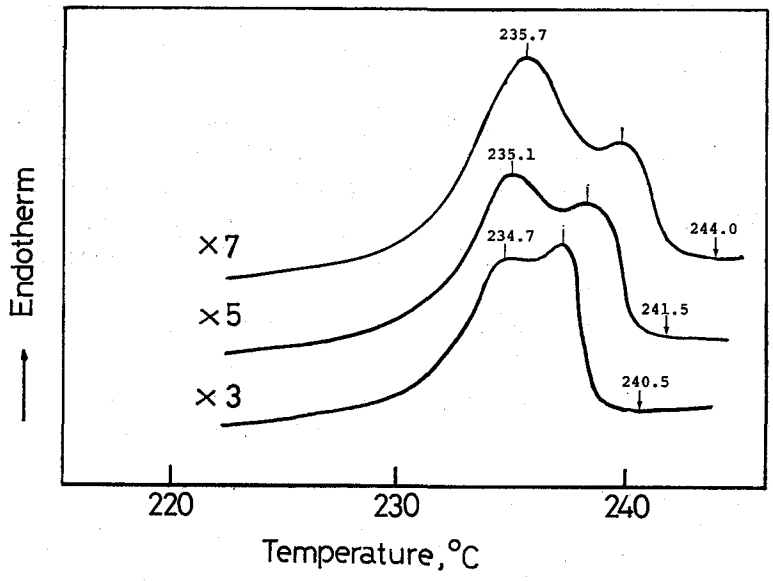

Fig. 5. DSC thermograms for PVA films stretched in the swollen state and annealed. The draw ratio is indicated to each curve.

232.8°C where a fusion peak is recognized for an unstretched well-crystallized PVA (see Fig. 4). The other appears in a range of temperatures much higher than the normal melting point of PVA. The melting points where the fusion finally terminates are determined to be 240.5, 241.5, and 244.0°C for the three-, five-, and seven-fold stretched samples, respectively (see Fig. 5 with the melting points listed in Table II).

Similar dual or multiple fusion curve is sometimes reported for other polymers such as polyethylene,[20~22] polyethylene terephthalate,[23] and nylon-66[24] together with an abnormally high melting temperature, when the polymers are crystallized under very high pressure or under conditions involving molecular orientation. Also for PVA such abnormally high melting temperature is reported by Mochizuki *et al*,[19] Yamaura *et al*,[25] and Monobe *et al*,[26] when the polymer is crystallized from the aqueous solution under high degree of stirring but such dual peak never has been recognized up to date. Thus we should note that the mode of stretching and subsequent crystallization for PVA examined in this paper brings very characteristic unique feature in the structure of the polymer. The dual fusion curve as well as abnormally high melting point are generally characteristic for samples, regardless of polymer sort, which were crystallized under condition involving molecular orientation and those should indicate dual structure or the presence of very highly ordered crystalline phase with large dimensions in the samples.

However, we point out here a very intimate similarity in the fusion behavior between the swell-drawn PVA samples and the lightly cross-linked polyethylene gel[4] which was crystallized from the molten and stretched or compressed state. Very distinct dual fusion curve is reported for the sample that was obtained from a molecular weight fraction with a very large molecular weight with minimum amount of cross-linkings. Since this sample indicates a very good rubbery elasticity in the molten state,

the crystallization from the molten and compressed state is considered to comprise two kinds of crystallization, the mechanism of which is quite different with each other. The first one is the crystallization from stretched molecular chains. It proceeds with a very enhanced rate because of the elevation of the equilibrium melting temperature (and hence increase of supercooling) due to the decrease of entropy change in the transformation by stretching. It produces highly ordered crystallites with larger dimensions associated with the higher melting temperatures, remaining a part of the molecular chains in an unstretched state. After this crystallization terminates with dissipation of stretched molecular chains, the other kind of crystallization takes place from less- or non-stretched molecular chains in the structure. It produces less ordered crystallites with smaller dimensions associated with lower melting temperatures in a normal range of melting of the polymer. Thus it is concluded together with data of molecular mobility or molecular orientation obtained by NMR[7] or birefringence[2] studies that the highly ordered crystalline region or crystallites with larger dimension coexist with less-oriented amorphous molecular chains in a relaxed state with smaller size of crystallites. The dual fusion behavior for this cross-linked polyethylene is well understood by the dual crystalline structure produced by the above-mentioned mode of crystallization.

For the swell-drawn PVA samples, there is no chemical cross-linkings in the molecular structure. However, as was pointed out in the introductory section, since the polymer molecules are thought to be stretched in accordance with the macroscopic stretching in the swollen state due to rather strong intermolecular attractive forces, the structure will have been brought about from thus stretched molecular chains in the course of deswelling, drying, and annealing. Thus a crystalline structure that corresponds to the dual fusion behavior will be brought about in a similar mechanism of crystallization as cross-linked polymers cited above. It should be concluded for the swell-drawn PVA samples that highly ordered crystallites with larger dimension coexist with smaller size of crystallites. As can be seen in Fig. 3, however, the total birefringence at room temperature for these highly drawn samples is larger than that for samples drawn in air. If less-oriented amorphous chains exist with the highly ordered crystallites in the structure, the total birefringence could not be so large as observed, since the higher orientation of the crystallites is not thought to compensate all of lowering in the birefringence by the amorphous chains. Therefore, it cannot be concluded that the highly ordered crystallites coexist with less-oriented amorphous chains at room temperature. Nevertheless, the extraordinarily high melting points of these samples still suggest such coexistence. Thus we reach a conclusion that the highly ordered crystallites coexist with crystallites with smaller size in the absence of relaxed amorphous chains at room temperature but melting of the latter crystallites at high temperatures produces less-oriented amorphous molecular chains in the course of fusion. The amorphous chain thus produced will be in equilibrium with the highly ordered crystallites in the time-scale of the DSC measurement.

In Table II, listed are the enthalpy of fusion for the drawn samples estimated from the fusion curves with planimetry. There is no noticeable difference between two series of swell-drawn samples which were stretched in the swollen state and then dipped in either methanol or acetone and annealed after drying. But as is expected

Table II. Melting Point and Heat of Fusion of Drawn and Annealed PVA Films

Sample	Draw ratio	Melting point Tm (°C)	Heat of fusion ΔH (cal/g)
	—	236.5	15.3
	2	236.2	17.5
Stretched in air	3	237.5	18.1
at 120°C and	4	239.8	18.6
annealed	5	239.5	19.3
	6	240.5	19.8
	7	240.5	19.9
	2	239.2	19.7
Stretched in the	3	240.5	20.6
swollen state	4	241.0	21.3
and annealed	5	241.5	22.4
(MeOH)*	6	243.0	22.8
	7	244.0	23.1
	4	240.6	20.6
Stretched in the	5	241.3	22.4
swollen state	6	241.0	22.6
and annealed	7	243.0	23.0
(acetone)**			

* Dipped in methanol before annealing
** Dipped in acetone before annealing

from the density data cited in the former section the quantities for the swell-drawn samples are appreciably greater than those for the heat-drawn samples of a same draw ratio. If the enthalpy of fusion is devided by the value for the perfectly crystalline phase of the polymer, 37.3 cal/g obtained by Tubbs[27] from the melting point measurement of the polymer-diluent system, a quantity correspond to the degree of crystallinity will be obtained.

In Fig. 6 the quantity thus obtained is plotted as the degree of crystallinity $(1-\lambda)_{\Delta H}$ against the value $(1-\lambda)_d$ derived from the density measurement. In such plot for crystalline polymers it is generally observed that as the value of $(1-\lambda)_d$ decreases the data progressively departs from the straight line of $(1-\lambda)_{\Delta H}=(1-\lambda)_d$ due to the contribution from the interfacial domain between the crystalline and amorphous phases in the structure.[28] As can be seen by the open circles in the figure the data for the swell-drawn samples indicates such tendency. It implies the coexistence of the well-defined pure crystalline and amorphous phases with the interfacial domain as is predicted from the afore-mentioned consideration of the fusion behavior. On the other hand, the $(1-\lambda)_{\Delta H}$ for the heat-drawn samples is appreciably smaller than that for the swell-drawn samples and shows no such tendency. This implies either greater contribution from the interfacial domain due to the complexities of its structure as is predicted from the mechanism in forming of the crystalline structure or less-defined crystalline and amorphous phases. However, further consideration of these data should be awaited until more reliable definite quantities about the density and enthalpy change

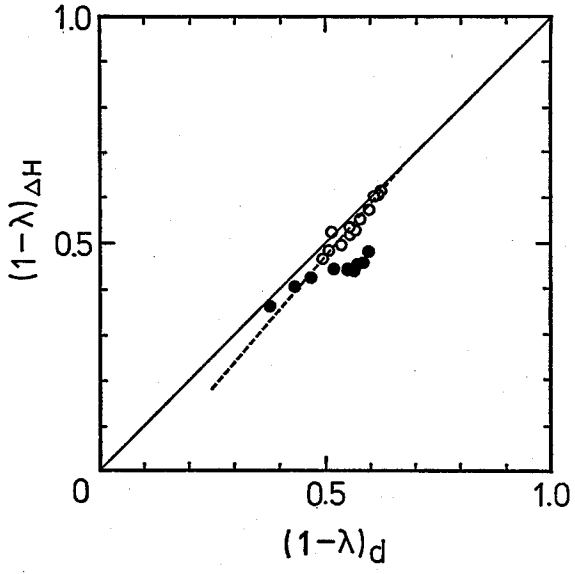

Fig. 6. Crystallinities for drawn PVA films, estimated from enthalpy of fusion and density. Open and closed circles show the data for annealed samples stretched to various degrees in the swollen state and those stretched in air at 180°C, respectively. The dotted line is drawn for the open circles.

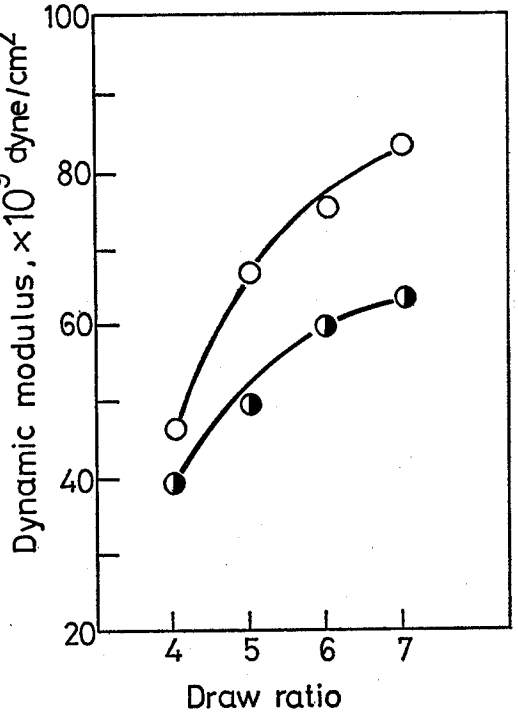

Fig. 7. Dynamic modulus *vs.* draw ratio for annealed PVA films stretched either in the swollen state or in air at 180°C. Open and half closed circles show the data for the former and latter samples, respectively.

of fusion for the perfectly crystalline phase of the polymer become available since it evidently depends on these quantities.

Dynamic Modulus

The dynamic moduli for the swell- and heat-drawn samples measured at room temperature by a frequency of 110 cps are plotted in Fig. 7 against draw ratio. As can be seen, the moduli for the swell-drawn samples not only increase with increasing of draw ratio but also those are about 30% greater than that for the heat-drawn samples. This is in good agreement with a prediction from the high degree of molecular orientation as well as the existence of the pure highly ordered crystallites with a larger dimension.

Shrinkage with Heating

In Figs. 8 and 9 the shrinkage with heating in air or water for the samples drawn sixfold under different conditions is plotted against temperature. As can be seen in the figures, the temperature where appreciable shrinkage initiates for the swell-drawn sample is about 40° higher than that for the heat-drawn samples. It shrinks appreciably only above 190°C and 95°C in air and water, respectively. In particular it does not shrink to only few percents in water at 100°C. This excellent dimensional stability for heating is not only surprising if one considers the hydrophilic molecular character of the polymer, but also it is very useful in the practical application. Since, as is discussed repeatedly, in this sample the highly ordered crystallites coexist with less-oriented amorphous chains after major melting of crystallites of smaller size completes, the shrinking will do not complete until the melting or dissolution finally terminates.

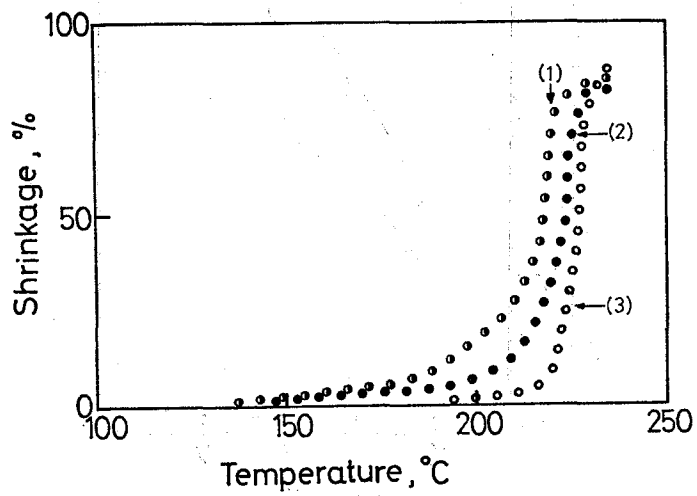

Fig. 8. Thermal shrinkage in air vs. temperature for sixfold stretched and annealed PVA samples. Curves; (1) stretched in air at 120°C (half closed circles), (2) stretched in air at 180°C (closed circles), (3) stretched in the swollen state (open circles).

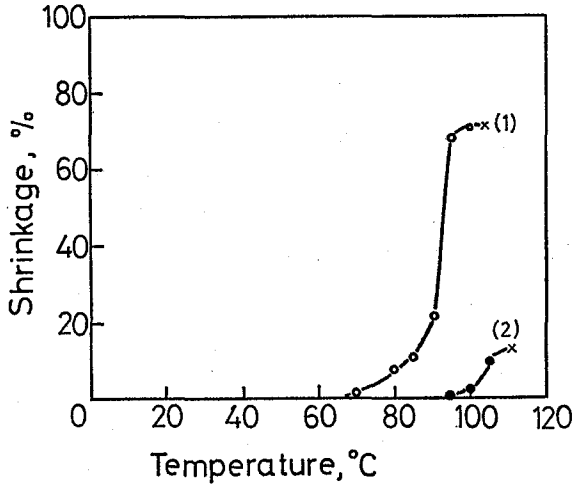

Fig. 9. Thermal shrinkage in water *vs.* temperature for sixfold stretched and annealed samples. Curves; (1) stretched in air at 180°C (open circles), (2) stretched in the swollen state (closed circles). The cross marks show the point where the test piece broke.

CONCLUSION

It has been evidently shown that if the molecular fraction of PVA is stretched to a high extent in the swollen state in water and annealed after replacing of the water with acetone or methanol and drying, the resultant product is generally associated with various characteristic properties such as high degree of molecular orientation and extraordinarily high melting point with excellent dimensional stability for heating. The detailed crystalline structure of the product is supposed, as is discussed repeatedly in the experimental section particularly concerning the fusion behavior, to be such that a highly ordered crystallites with larger dimension coexist with less-ordered crystallites with smaller size and at higher temperatures with less-oriented amorphous molecular chains. This characteristic crystalline structure of the product resembles that of lightly cross-linked polymers such as polyethylene, isotactic polypropylene, and polyvinylidene fluoride which show rubbery elasticity in the molten state, when these are crystallized from the molten and stretched or compressed state involving molecular orientation.

The crystallization mechanism of these cross-linked polymers has been extensively studied and general feature of the crystallization under conditions involving molecular orientation is elucidated in detail.[1~10] In despite of the absence of chemical cross-linkings, formation of the crystalline structure of PVA in the manner employed is thought to have been conducted as if the crystallization was carried out from the molten and elastically stretched molecular chains in the experimental time-scale due to the strong intermolecular attractive forces cited repeatedly. Thus the very characteristic properties of the PVA sample is well understood as a general feature when cross-linked polymers are crystallized from the molten and stretched state.

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